ANODIZING MAGNESIUM

Herbert K. De Long, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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The invention relates to baths for and method of treating light metal articles particularly those of magnesium and the magnesium-base alloys to produce thereon a coating which affords protection against corrosion. It more particularly concerns an improved anodic coating method by which articles of magnesium and the magnesium-base alloys are given a hard strongly adherent coating affording protection against corrosion. The term "magnesium-base alloy" used herein means an alloy of magnesium in which the magnesium content is at least 80 percent by weight.

Magnesium and the magnesium-base alloys, like other structural metals, oftentimes are subjected to corrosive conditions in use and numerous methods of treatment have been proposed heretofore in efforts to provide the surface of these metals with corrosion resistant coatings to prevent the underlying metal from being attacked. Yet, in spite of these efforts, no highly corrosion resistant coatings have become commercially available. As a consequence, it is a desideratum of the art to provide coatings for magnesium and its alloys having improved resistance to corrosion in comparison with available coatings. Accordingly, it is an object of the invention to provide a bath for and method of coating magnesium and its alloys which fulfills the foregoing need. Other objects and advantages will appear as the description of the invention proceeds.

The invention is predicated upon the discovery that by anodizing magnesium and magnesium alloy articles in a hot aqueous acidic solution containing dissolved chemical compounds consisting, at least ammonium, fluorine, phosphate, sodium, and hexavalent chromium, at a voltage sufficient to produce sparking at the surface of the articles in the solution, highly corrosion resistant coatings are obtained in a short time. The coatings are nominally of a tan to an olive green color. In addition to strongly resisting corrosion, as from the atmosphere and salt water, the coatings are strongly adherent, hard, and resistant to damage by abrasion. The coatings also form an advantageous base on which to apply paint, varnish, enamel, and lacquer since the coatings are free from the alkali, usually present in conventional protective coatings applied to magnesium-base alloys, which contributes to premature paint failures.

The invention then consists of the improved anodizing bath composition and method of anodizing articles of magnesium and the magnesium-base alloys herein fully described and particularly pointed out in the claims.

In carrying out the invention, the articles to be coated are anodized in a bath which consists of a slightly acid aqueous solution, the pH being not over 4 but preferably about 0.5 to 2, containing the radicals ammonium, fluorine, phosphate, sodium, and hexavalent chromium in solution. The necessary acidity may be derived generally from the chemical compounds which are dissolved in the bath to contribute to it the essential radicals referred to above, namely, ammonium, fluorine, phosphate, sodium, and hexavalent chromium, as when acids or acid salts having the foregoing radicals in combination are used in the bath or by the addition of a strong mineral acid not involving the foregoing radicals, for example, sulfuric acid, nitric acid, or hydrochloric acid. However, it is generally preferable to rely upon the chemical compounds comprising the aforesaid radicals, which are used in formulating the bath, to render the bath sufficiently acid, as will become apparent on considering the various combinations of chemical compounds which are suitable for the purpose as in the following examples of such compounds.

For supplying the fluorine or fluoride radical of the bath, there is dissolved in the bath a soluble fluoride. Since the bath must also contain sodium as well as ammonium, it is advantageous to use either sodium fluoride or ammonium fluoride since these chemical compounds contribute either sodium or ammonium as the case may be as well as the fluoride radical. The fluorides used advantageously may be in the form of acid salts, for example, NaFHF and NH₄FHF, which can serve to acidify the bath, as indicated above, as well as provide the desired fluoride radical. Hydrofluoric acid may be used to provide the fluoride radical. Insofar as the fluoride radical is concerned, its concentration should be at least 6 percent by weight of the bath and may be as high as 25 percent that producing a saturated solution in the presence of the remaining constituents of the bath. In this connection, it will be understood that two or more fluorides may be used at the same time to achieve the desired fluoride concentration as for example by using both sodium fluoride (or biliurate) and ammonium fluoride (or biliurate). The maximum concentration of the fluoride radical, which can be attained is largely limited by the necessary presence of the sodium radical which brings about precipitation of sodium fluoride when its solubility is exceeded.

Undissolved fluoride may be present in admixture with the bath without detriment, although it is preferable to use only sufficient fluoride in the presence of the dissolved sodium radical to provide at least 6 percent of dissolved fluoride without attaining saturation with respect to sodium or other fluoride.

For supplying the sodium radical, there is dissolved in the bath a suitable soluble sodium compound, for example Na₂SO₄ although the sodium compound used may also at the same time provide a portion of the desired fluoride content of the bath, as already indicated, as when the sodium salt used is sodium fluoride, or a portion of the desired hexavalent chromium content as when the sodium salt used comprises a soluble hexavalent chromium compound or a portion or all the desired phosphate content as when the sodium salt used comprises a soluble phosphate. The following sodium compounds in addition to those already mentioned may be used appropriately to provide all or a part of the necessary sodium radical: Na₃Crosal, Na₃PO₄, Na₂H₂PO₄, NH₄OH, Na₂H₂PO₄, NH₄OH, Na₂H₂PO₄, H₂O, Na₃PO₄, Na₂H₂PO₄, H₂O, Na₃PO₄, Na₂H₂PO₄, H₂O, Na₃PO₄, Na₂H₂PO₄, H₂O.

The sodium content of the bath should exceed about 0.3 percent and may be as high as 3 or 5 percent by weight. In the lower ranges of the sodium content, it is apparent that if the sodium is derived from sodium fluoride additional fluoride would need to be supplied by some other soluble fluoride to produce a sufficient fluoride concentration in the bath to meet the minimum fluoride requirement of 6 percent.

Since the bath must also contain the ammonium radical, the fluoride may advantageously be as the normal or acid ammonium fluoride and thereby furnish part or all of the fluoride requirement as well as part or all of the NH₄ requirement which is to be at least 3.2 percent and may be as much as 15 percent by weight of the bath. Other ammonium compounds may be used for supplying the necessary ammonium radical, for ex-
ample, those which furnish other needed radicals besides NH₄ such as the ammonium phosphates and the ammonium chromates. Ammonium hydroxide may be used as the ammonium source in which case it becomes acidified in the bath in view of the necessity to maintain the pH of the bath between 0.5 and 4.

The phosphate content of the bath calculated as PO₄ is to be between 2 and 10 percent by weight and may be derived from the alkali metal and ammonium ortho- and pyrophosphates and ortho- and pyrophosphoric acids, and, as already mentioned, some of these phosphates may contribute some or all of the required amount of the sodium radical as well as more or less of the required NH₄. Among the phosphates which may be used as the source of phosphates are: H₃PO₄, H₂PO₃, NaH₂PO₄, NH₄H₂PO₄, (NH₄)₂PO₄, Na₃PO₄, and Na₅PO₄, and Na₅H₄PO₄.

The hexavalent (equivalent) chromium content of the bath, which is to be 0.3 to 5 percent by weight of the bath, may be derived from any soluble hexavalent chromium compound, as for example, Na₂Cr₂O₇, Cr₂O₃, Na₂Cr₂O₇, and (NH₄)₂Cr₂O₇. As in the case of the other compounds used in the bath, the hexavalent chromium compounds used may also furnish part or all of the sodium and a part of the ammonium radical requirements of the bath.

In anodizing articles of magnesium and the magnesium-base alloys in accordance with the invention, the anodizing bath prepared as above described, so as to contain the desired concentration of each of the radicals NH₄, F, PO₄, Na, and Cr, and a pH of 0.5 to 4, is maintained at a temperature between 150° F. and the boiling point of the bath during the anodization. A preferred operating temperature is 155° to 165° F. The article to be anodized is immersed in the bath which is then electrolyzed using the article as the anode. A.C. or D.C. may be used, A.C. being preferred, although its use requires about 30 percent more time to complete the coating than D.C.

The voltage applied to the article is determined by the current density it is desired to produce at the surface of the article and is gradually increased during the anodization from a low value at the beginning, when the resistance to the passage of current is low, to higher values as the resulting anodic coating develops and becomes thicker, harder, and more electrically resistant as the anodization proceeds. Only relatively soft coatings having a grey color and useless for corrosion protection form at applied voltages less than those producing a characteristic sparking or arcing phenomenon which occurs between the surface of the article and the bath when the voltage attained during anodization exceeds about 70 to 75 volts. Accordingly, as the anodization proceeds, the applied potential is progressively increased to and beyond the sparking voltage and thereafter is maintained at a value which continuously produces a substantial current flow with sparking until the desired thickness of coating is obtained. After the sparking voltage is attained, the color changes from grey to tan for light thickness of the coating and finally to an olive green for the thicker coatings. Effective thicknesses of coating are 0.0012 to 0.0015 inch, but other thicknesses may be produced. The voltage thus applied need not exceed about 120 volts. The magnesium-base alloys containing a relatively small amount, for example, less than 5 percent of non-magnesium metal require the application of a higher voltage than the magnesium-base alloys containing a relatively higher content, for example, 10 percent of non-magnesium metal. With these alloys, good coatings are obtained with 75 to 85 volts. The duration of the anodization after the sparking voltage is reached is not sharply critical and may be from 5 to 30 minutes or more depending upon the current density used and the coating thickness desired. Satisfactory coatings have been obtained using from 250 to 350 amperes per square foot of surface anodized with current densities of upwards of 2 amperes per square foot of anodized surface. A larger number of amperes minutes, for example 600, does not appear to yield more corrosion resistant coatings. For example, there may

Table I

<table>
<thead>
<tr>
<th>Compound Used</th>
<th>Radicals Calculated Total Wt. Percent</th>
<th>pH</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. Percent</td>
<td>Formula</td>
<td></td>
<td>Current Density, amp/sq. ft.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Time, Min.</td>
</tr>
<tr>
<td>1.</td>
<td>NH₄H₂F₄PO₄</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>2.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>3.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>4.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>6.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>7.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>8.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>9.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
<tr>
<td>10.</td>
<td>Na₃Cr₂O₇</td>
<td>7.1</td>
<td>20</td>
</tr>
</tbody>
</table>

A.C. = Alternating current of 60 cycles.
D.C. = Direct current.
be used a current density of 15 amperes per square foot for 20 minutes. This time includes the time taken
to reach the voltage at which sparking occurs (that is 70
to 75 volts) which is usually not more than one to three
minutes at such current densities and the balance of the
time is taken up in the anodization while sparking
during which the hard corrosion resistant coating of the
invention is produced.

The practice of the invention is illustrated in the ex-
amples set forth in Table I showing various anodizing
bath compositions and conditions under which anodiza-
tions in accordance with the invention were made.

In Table I, the anodizations with each bath were
made with test panels of a magnesium-base alloy sheet
0.04 inch thick having the nominal composition of 3
percent Al, 1 percent Zn, 0.3 percent Mn, the balance
magnesium. The panels anodized in baths 1 to 7, inclu-
sive, were pickled before anodization in 7 percent aque-
ous nitric acid solution for 30 seconds at 76° F. The
panels used in baths 8 and 10, inclusive, were anodized
without a previous cleaning. In each instance, the panels
on being anodized were a uniform coating of more
or less olive green color which was hard and strongly
resistant to corrosion as determined by a salt solution
spray test. In testing the corrosion resistance of the
panels, they were placed in a spray chamber with one
side facing upward at an angle of 15 percent to the hori-
Zontal and subjected to a spray of 20 percent sodium
chloride solution (water solution) at 95° F. produced
by air atomization of the solution onto the panels. The
spraying was continued for 200 hours. The top face of
each sprayed panel was examined to determine the pro-
portion of the area, if any, which was attacked by the
spray after 24 hours and after 200 hours of the spray
 treatment. The results of these examinations are set
forth in Table II.

### Table II

<table>
<thead>
<tr>
<th>Bath No.</th>
<th>Salt Spray Corrosion Test: Percent of Area Attack at 95° F.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td>1</td>
<td>none</td>
</tr>
<tr>
<td>2</td>
<td>none</td>
</tr>
<tr>
<td>3</td>
<td>none</td>
</tr>
<tr>
<td>4</td>
<td>none</td>
</tr>
<tr>
<td>5</td>
<td>none</td>
</tr>
<tr>
<td>6</td>
<td>none</td>
</tr>
<tr>
<td>7</td>
<td>(i)</td>
</tr>
<tr>
<td>8</td>
<td>none</td>
</tr>
<tr>
<td>9</td>
<td>none</td>
</tr>
<tr>
<td>10</td>
<td>none</td>
</tr>
</tbody>
</table>

1 Not observed.

Among the advantages of the invention are that the
coating obtained is uniform in appearance and hides the
underlying metal; the coating hard and strongly resists
abrasion; the coating possesses extreme resistance to cor-
rosion; the bath effectively cleans the work as it is being
anodized, thereby obviating the need for the usual pick-
ling prior to the anodization; the coating produces an
enduring base for paint, varnish, lacquer, and enamel.

This application is a continuation-in-part of my co-
pending application Serial No. 332,495, filed January
21, 1953 (now abandoned).

1 claim:

1. An anodizing bath consisting of an aqueous solu-
tion of water-soluble inorganic compounds yielding in
the aqueous solution the radicals: ammonium, fluoride,
phosphate, sodium, and hexavalent chromium, the amount
by weight of the ammonium radical being between
3.2 and 15 percent, that of the fluoride radical being at
least 6 percent, that of the phosphate radical calculated
as PO₄ being between 2 and 10 percent, that of the sodi-
um radical being between 0.3 and 5 percent and that of
the hexavalent chromium radical being between about
0.3 and 5 percent, and sufficient mineral acid to give the
solution a pH between 0.5 and 4.

2. An anodizing bath according to claim 1 in which
the phosphate radical is derived from a phosphate se-
lected from the group consisting of the ortho- and pyro-
phosphates.

3. An anodizing bath consisting of a solution in water
of ammonium bifluoride, a sodium phosphate selected
from the group consisting of the ortho- and pyrophos-
phates, and a soluble hexavalent chromium compound,
in proportions such as to provide in the bath from 3.2
to 15 percent of the ammonium radical, at least 6 percent
of the fluoride radical, from 2 to 10 percent of the
phos-
of 0.3 to 5 percent; and a sufficient amount of a mineral acid to give the solution a pH of from 0.5 to 4, the anodizing being continued for a time sufficient to give the surface of the article a tan or green color.

9. An anodizing bath consisting of a solution in water of ammonium bifluoride, orthophosphoric acid and sodium dichromate, in proportions such as to provide in the bath from 3.2 to 15 percent of the ammonium radical, at least 6 percent of the fluoride radical, from 2 to 10 percent of the phosphate radical, PO₄, from 0.3 to 5 percent of the sodium radical, from 0.3 to 5 percent of hexavalent chromium, and sufficient mineral acid to give the solution a pH of 0.5 to 4.

References Cited in the file of this patent

UNITED STATES PATENTS
2,414,090 Buzzard 1947 Jan. 14

FOREIGN PATENTS
543,726 Great Britain 1942 Mar. 10
907,465 France 1945 July 2
Dedication


Hereby dedicates to the Public the remaining term of said patent.

[Official Gazette December 24, 1974.]